

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 November 2001 (15.11.2001)

PCT

(10) International Publication Number
WO 01/85854 A1

(51) International Patent Classification⁷: C09D 5/10, 183/02, 183/04

(21) International Application Number: PCT/EP01/05512

(22) International Filing Date: 11 May 2001 (11.05.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0011255.7 11 May 2000 (11.05.2000) GB
0110627.7 1 May 2001 (01.05.2001) GB

(71) Applicant (for all designated States except US): DOW CORNING CORPORATION [US/US]; Midland, MI 48611 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CLERICI, Vittorio [IT/DE]; Am Deutelsberg 9, 65375 Oestrich-Winkel (DE). WILHELM, Alexandra [DE/DE]; Merowingerstrasse 27, 55218 Ingelheim (DE). YAMASHITA, Jiro [JP/DE]; Steubenstrasse 32, 65189 Wiesbaden (DE).

(74) Agents: DONLAN, Andrew, M. et al.; Dow Corning Limited, Cardiff Road, Barry CF63 2YL (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(iii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG)
- of inventorship (Rule 4.17(iv)) for US only
- of inventorship (Rule 4.17(iv)) for US only
- of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/85854 A1

(54) Title: COATING COMPOSITION

(57) Abstract: A Chromium VI-free coating composition comprises a binder and a corrosion inhibitor in a solvent, wherein the binder comprises a silicate and an organic titanate, and the corrosion inhibitor comprises aluminium particles and zinc particles preferably flakes. The composition may also comprise an anti-corrosion additive which comprises metal phosphate, a lubricant which comprises a polyolefin wax, and/or a thickener. The coating composition is useful for coating substrates such as nuts, bolts and other fasteners, door, bonnet and boot lock parts, hinges, door stoppers, window guides, seat belt components, brake rotors and drums, and other transportation industry related parts.

- 1 -

COATING COMPOSITION

[0001] The present invention relates to a coating composition, for use in the protection of metal surfaces, 5 which comprises a binder, a corrosion inhibitor, and a solvent.

[0002] It is well known to treat metal surfaces such as iron and steel with some form of corrosion inhibiting treatment or coating. Corrosion inhibiting coatings are 10 well known in the art and generally contain metal particles in particular zinc and/or aluminium particles as active ingredients together with some form of binder.

[0003] GB 1380748 describes a coating composition particularly, but not exclusively, for a zinc filled coating 15 composition which when applied to a metal surface will provide galvanic protection to the metal. The composition comprises trialkoxysilanes which have been cohydrolysed and cocondensed with a hydrolysable titanium ester. The Silane is selected from $RSi(OR')_3$ and $RSi(OR''OR''')_3$ where R and 20 R' are monovalent aliphatic or aromatic hydrocarbon radicals having up to 10 carbon atoms, R'' is a divalent hydrocarbon radical having from 2 to 6 carbon atoms and R''' are monovalent aliphatic or aromatic hydrocarbon radicals having up to 10 carbon atoms or hydrogen.

[0004] GB 1499556 relates to a process for hydrolyzing 25 ethyl silicate to form a gellable liquid hydrolysate which is used for mixing with powders such as powdered zinc for use in an anti-corrosion paint. The ethyl silicate is acid hydrolysed and the solvent for the hydrolysis is acetone or 30 an alcohol

[0005] EP0808883 discloses a water-reducible coating composition for corrosion protection comprising particulate metal such as aluminium or zinc and a water reducible

- 2 -

organofunctional silane. Epoxy silanes, particularly beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and/or gamma glycidoxypropyltrimethoxysilane were preferred. Other constituents included a high boiling point organic liquid, a 5 water soluble cellulose based thickener and a wetting agent.

[0006] US 5393611 and US 5324545 both relate to a dip-coating method for protecting chromatised or passivated zinc coatings on steel or the like using a composition of a titanic acid ester and a "so-called" organofunctional 10 polysiloxane, preferably having between 2 and 10 siloxane repeating units and epoxy end groups. There is no clear definition of the meaning of the term organofunctional polysiloxane in either of these documents but it would seem to mean a polymer with a siloxane backbone having at least 15 one Si-R bond where R is an unsaturated or functionally substituted hydrocarbon radical. Confusingly however the examples in US 5393611 and US 5324545 both teach that rather than an organofunctional polysiloxane being used the preferred silicon containing compound is an epoxy silane, 20 namely gamma glycidoxypropyltrimethoxysilane.

[0007] The present inventors have found an increasing demand from industry for coatings for metal surfaces which can provide a high level of corrosion protection, cathodic protection, and "for-life" dry lubrication (i.e. the metal 25 surface needs coating only once during its working life) with defined and constant coefficient of friction, whilst being Chromium VI-free and providing an attractive appearance to articles coated with the coating. Commercially available coatings are unable to satisfy all of 30 these demands.

[0008] According to the present invention there is provided a coating composition which comprises a binder and a corrosion inhibitor in a solvent, wherein the binder comprises a silicate and an organic titanate, and the

- 3 -

corrosion inhibitor comprises aluminium particles and zinc particles.

[0009] The binder used in the composition of the present invention comprises a silicate and an organic titanate. For 5 the avoidance of doubt, it is to be understood that the term silicate is used to mean a compound which contains substantially no Si-C bonds, i.e. that carbon linkages to silicon in silicates as described in this invention are substantially always via an oxygen atom (i.e. an Si-O-C bond). Most preferably a silicate in accordance with this 10 invention contains no Si-C bonds. Preferably, the binder comprises 20 to 60% by weight (e.g. 30 to 45%) silicate, and 40 to 80% by weight (e.g. 55 to 70%) organic titanate to a total of 100% by weight.

15 [0010] Suitable silicates include colloidal silica and organic silicates, with the latter being preferred. Suitable organic silicates include silicate esters, for example silicate ester monomers (e.g. ethyl silicate), hydrolysate (e.g. silicic ester hydrolysate) and 20 alkoxy silanes, preferably tetraalkoxy silanes, although silicate ester polymers are most preferred, (e.g. alkyl polysilicates where the alkyl group has 1 to 6 carbon atoms and is most preferably methyl or ethyl).

25 [0011] Suitable organic titanates include titanate chelates (e.g. titanium acetylacetone and triethanolamine titanate) and titanate esters, with the latter being preferred. Suitable titanate esters include titanate ester monomers (e.g. tetraalkyl titanates wherein each alkyl group is the same or different and contains between 1 and 12 30 carbon atoms, examples include tetrabutyl titanate, tetraisoctyl titanate, and tetraisopropyl titanate), although titanate ester polymers are preferred (e.g. alkyl poly titanates such as butyl poly titanate).

- 4 -

[0012] The corrosion inhibitor used in the composition of the present invention comprises aluminium particles and zinc particles. The aluminium particles may be in the form of powder, paste or flake, with aluminium flake (leafing or non-leafing) being preferred. The aluminium particles preferably have an average particle size of 4 to 20 μm , more preferably 6-15 μm . The zinc particles may be in the form of zinc powder, for example zinc spheres or zinc flake, preferably zinc flake. The zinc particles preferably have an average particle size of 6 to 26 μm , more preferably 8-15 μm . The corrosion inhibitor preferably comprises 80 to 97% by weight (e.g. 87 to 95%) of zinc particles, and 3 to 20% by weight (e.g. 5 to 13%) of aluminium particles to a total of 100% by weight.

[0013] The composition of the present invention may also comprise a metal phosphate as an anti-corrosion additive. Preferred metal phosphates are zinc phosphates, including modified zinc orthophosphates (e.g. modified zinc aluminium-orthophosphatehydrate) and modified zinc polyphosphates (e.g. modified zinc aluminium-polyphosphate hydrate), with the latter being most preferred. The metal phosphate may be present in an amount of up to 33% by weight of the solid content of the composition of the present invention (i.e. without the solvent), preferably 5 to 20% by weight.

[0014] The composition of the present invention may further comprise a thickener, e.g. silica and/or organic modified clay, in an amount of up to 4% by weight of the solid content of the composition, preferably from 1 to 3% by weight.

[0015] The composition of the present invention may still further comprise a lubricant, for example a wax, including hydrocarbon waxes and polytetrafluoroethylene (PTFE) wax, preferably a polyolefin-containing wax (e.g. micronised

polypropylene hydrocarbon wax), in an amount of up to 8% by weight of the solid content of the composition, preferably from 1.5 to 4.5% by weight.

[0016] Suitable solvents for use in the composition of the present invention are well known in the art. Organic solvents are suitable, including alcohols (e.g. methanol, ethanol, propanol, butanol), ketones (e.g. acetone, methyl ethyl ketone, methyl butyl ketone, cyclohexanone), esters (e.g. butyl acetate), and mixtures thereof. However, preferred solvents for the coating composition are hydrocarbon solvents, in particular white spirits, due to their high evaporation rates and low levels of aromatic compounds. Particularly preferred white spirits are those containing C₁₁-C₁₆ normal, iso- and cycloalkanes.

[0017] The coating composition of the present invention thus comprises a binder and corrosion inhibitor in a solvent, and preferably a metal phosphate anti-corrosion additive, a lubricant, and a thickener. Preferably, the solid content of the composition comprises 50 to 80%, more preferably 65 to 80 %, by weight corrosion inhibitor, 9 to 18%, more preferably 11 to 16%, by weight of binder, up to 33%, more preferably 5 to 20% by weight of metal phosphate, up to 8%, more preferably 1.5 to 4.5% by weight of lubricant, and up to 4%, more preferably 1 to 3% by weight thickener.

[0018] The coating composition of the present invention can be prepared by mixing its components together using conventional apparatus, preferably by first blending some of the solvent and binder, then adding the corrosion inhibitor, and then finally adding the remaining solvent.

[0019] The coating composition of the present invention may be applied to a surface by any conventional application technique, for example brushing, dip-spinning dipping, and

- 6 -

spraying (e.g. by aerosol can). Other common application methods include spraying drums, centrifuges, electrostatic or automatic spraying, printing and roller coating. The chosen method of application will depend upon the shape, 5 size, weight and quantity of items to be coated. Preferably, 2, 3 or more coating layers are applied. The coating thickness has an influence on the life and properties of the resulting coating, and should be greater than the roughness of the surface, typically from 5 to 25 μ m. 10 Once the surface has been coated with the composition, it is dried to evaporate the solvent and cure the coating. The coating composition can be cured by, for example, heating at 200°C for 10 minutes.

[0020] The coating composition of the present invention 15 may be used alone or in combination with other commercially available anti-friction or anti-corrosive coatings. A preferred commercially available anti-friction coating which may be utilised in combination with the composition of the present invention has the following composition (percentages 20 by weight), and is referred to hereinafter as "top-coat A":

20-25% lubricant - mixture of phenolic, epoxy and vinyl butyral resins, and PTFE.

25 70-75% solvent - mixture of methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone.

[0021] The coating composition of the present invention may be used in combination with a metal particle free top-coat hereafter referred to as "top-coat B" comprising a 30 silicate as herein before described and an organic titanate as herein before described. The top-coat may optionally include any other components as herein before described for the coating composition of the present invention other than

the metal (i.e. zinc and aluminium) particles. The top-coat is described in the applicants co-pending patent application GB 0110627.7.

5 [0022] Particularly preferred combinations of coating layers include:

- 1) 1, 2 or 3 coating layers of the composition of the present invention.
- 2) 1, 2 or 3 coating layers of the composition of the present invention followed by 1 to 3 coating layers 10 of top-coat B
- 3) 1 or 2 coating layers of the composition of the present invention followed by 1, 2 or 3 coating layers of top-coat A.

Another possibility is the combination of all three 15 coatings, i.e. 1 or 2 coating layers of the composition of the present invention followed by 1, 2 or 3 coating layers of top-coat A and finally followed by 1 to 3 coating layers of top-coat B, although this combination is highly unlikely to be utilised for reasons of cost alone.

20 [0023] Substrates may be pretreated prior to coating with the coating composition of the present invention to improve adhesion and life of the resulting protective coating. Conventional methods of pretreatment include degreasing (for example, using solvents or steam), treatment of corroded 25 surfaces by acid or alkali, phosphating, oxalic acid treatment of stainless steel, sandblasting and anodizing.

[0024] The coating composition according to the present invention can thus be used to provide a protective coating, for metals prone to corrosion, such as iron and steel. The 30 provision of a protective coating on a substrate will result in high corrosion resistance, cathodic protection, and, when a lubricant is utilised, for-life lubrication with a defined and constant coefficient of friction for articles such as

- 8 -

automotive components is provided, for example nuts, bolts and other fasteners, door, bonnet and boot lock parts, hinges, door stoppers, window guides, seat belt components, brake rotors and drums, and other transportation industry 5 related parts.

[0025] A further embodiment of the present invention relates to a substrate coated with the coating composition as hereinbefore described and to a method of coating such a substrate with a coating composition as hereinbefore 10 described .

[0026] The present invention will now be illustrated by way of example. All percentages are by weight.

Example 1

15

[0027] A coating composition according to the present invention was prepared by mixing the following materials:

8% ethyl silicate polymer
20 13% polybutyl titanate
3% aluminium pigment
33% zinc pigment
5% zinc-aluminium phosphate
34% petroleum white spirit
25 2% polypropylene wax
0.6% silica
0.6% organic modified clay

Example 2 - substrate pretreatment

30

[0028] Steel bolts, 10 mm diameter by 60 mm in length, were pretreated by sandblasting.

- 9 -

Example 3 - substrate coating

[0029] The pretreated bolts of Example 2 above were coated with coating compositions AF1 to AF3 below. Each 5 coating layer was applied by dip spinning in a centrifuge, partial curing for 10 minutes at 200°C, followed by further dip spinning and full cure at 200°C for 10 minutes.

AF1 - 2 coating layers of the coating composition of Example 1 alone.

10 AF2 - 3 coating layers of the coating composition of Example 1 alone.

AF3 - 2 coating layers of the coating composition of Example 1 followed by 2 coating layers of Coating A described hereinabove.

15 [0030] A comparative anti-friction coating (CAF1) was also prepared which consists of 3 coating layers of Coating A described hereinabove.

Example 4 - corrosion resistance

20

[0031] Salt spray test DIN 50021 was performed on the AF1 to AF3 bolts prepared according to Example 3 above. The results are shown in Tables 1 to 3 below (average results taken from test results for 10 bolts):

25

- 10 -

Table 1 - coating AF1

		% red rust corrosion	
Test	Time (hours)	Thread	Head
1	480	0.0	0.0
	900	0.0	0.0
2	480	0.0	0.0
	900	0.0	0.0
3	480	0.0	0.0
	900	0.0	0.0
4	480	0.0	0.0
	900	0.0	0.0

Table 2 - coating AF2

		% red rust corrosion	
Test	Time (hours)	Thread	Head
1	480	0.0	0.0
	720	0.0	0.0
	> 900	0.0	0.0
2	480	0.0	0.0
	720	0.0	0.0
	> 900	0.0	0.0
3	480	0.0	0.0
	720	0.0	0.0
	> 900	0.0	0.0
4	480	0.0	0.0
	720	0.0	0.0
	> 900	0.0	0.0

- 11 -

Table 3 - coating AF3

		% red rust corrosion	
Test	Time (hours)	Thread	Head
1	480	0.0	0.0
	900	0.0	0.0
2	480	0.0	0.0
	900	0.0	0.0
3	480	0.0	0.0
	900	0.0	0.0
4	480	0.0	0.0
	900	0.0	0.0

Example 5 - lubrication

5 [0032] The coefficient of friction of the AF1 and AF3 coated bolts prepared according to Example 3 above was determined using an Erichsen AP 541 Bolt Testing Machine. Testing was performed on bolts having been tightened 1 and 3 times and against different surfaces. The results are shown 10 in Table 4 below:

- 12 -

Table 4

Coating	Surface	Tightenings	Total coeff. of friction	± variation
None	Steel	1	0.195	0.035
AF1	Steel	1	0.112	0.003
AF1	Steel	1	0.123	0.005
AF1	Painted steel	1	0.129	0.008
AF1	Aluminium	1	0.138	0.003
AF1	Steel	3	0.114	0.003
AF1	Steel	3	0.127	0.007
AF1	Painted steel	3	0.131	0.009
AF1	Aluminium	3	0.140	0.004
AF3	Steel	1	0.114	0.006
AF3	Steel	1	0.100	0.006
AF3	Painted steel	1	0.109	0.008
AF3	Aluminium	1	0.104	0.002
AF3	Steel	3	0.114	0.009
AF3	Steel	3	0.108	0.013
AF3	Painted steel	3	0.114	0.012
AF3	Aluminium	3	0.114	0.007

Example 6 - cathodic protection

5 [0033] Unpretreated iron panels were degreased and coated on one side with the coating composition of Example 1 above and with the anti-friction coating CAF1 using an Erichsen spiral film applicator. The panels were then cured for 10 minutes at 200°C. After cooling, the dry thickness of the 10 cured coatings was measured. Corrosion protection tape was then applied to the untreated surfaces of each panel and an

- 13 -

X-cut made in the coated surface of each panel until the metal surface was reached. The panels were then placed into a salt spray tester (DIN 50021) until red rust formation was noticed, and the results are given in Table 5 below:

5

Table 5		
AF coating	Thickness (μm)	red rust formation after [hours]
Example 1	4	144
Example 1	7.5	312
CAF1	10	24

Example 7

[0034] Bolts of the type described in example 2 were 10 coated with 2 layers of the coating composition of example 1 and cured as described in Example 3. After curing the coated bolts were provided with two alternate top-coats of the type referred to above as coating B. The top-coat compositions were prepared by mixing the materials 15 identified in Table 6 as follows:-

The polybutyl titanate and ethyl polysilicate were added into a mixing kettle with a dissolver disk for a period of 10 minutes. Simultaneously a slurry of the silica, clay zinc-aluminium phosphate and, when present, polypropylene 20 wax in a proportion of the Petroleum white spirit (about 9% by weight of solvent in sample 2 and about 20 % by weight of solvent in example 1) was prepared in an Ultra turrax homogeniser. The slurry was then added into polybutyl titanate and ethyl polysilicate mixture and the resulting 25 mixture was mixed with the dissolver disk for a period of 30 minutes at which time the residual amount of solvent was added and the final mixture was mixed in the presence of the

- 14 -

dissolver disk for a further 10 minutes. It will be seen that sample TC1 omits the anti-corrosion additive zinc-aluminium phosphate.

Table 6

Component	Weight %	Sample TC1
Petroleum white spirit	47.45	43.61
Polybutyl titanate	24.34	22.38
Ethyl polysilicate	24.34	22.38
Silica	1.15	1.06
Organic modified clay	1.00	0.91
zinc-aluminium phosphate	0.00	8.08
Polypropylene wax	1.72	1.58
complete:	100.00	100.00

5

[0035] The top-coat compositions, samples TC1 and TC2 were applied in an identical fashion to the coating composition of the present invention and each layer applied was cured at 200°C for 10 minutes.

10

Example 8 - corrosion resistance

[0036] Salt spray test DIN 50021 was performed on the bolts prepared as discussed in Example 7. The results are 15 shown in Table 7 below (average results taken from test results for 10 bolts). In each test two layers of the coating composition in accordance with the invention were coated on to each bolt but the number of layers of the alternative top-coats was varied as indicated in Table 7:

20

Table 7 - Corrosion resistance (with top-coat)

Coating	Time (hours)	% of red rust on head of bolt
Coating 8.1 (no top-coat)	900	0.0
Coating 8.2 (1 layer of TC1)	2000	1.7
Coating 8.3 (1 layer of TC2)	2000	0.0
Coating 8.4 (2 layers of TC1)	2000	1.0
Coating 8.5 (2 layers of TC2)	2000	0.0

[0037] The above should be compared with the results provided in Table 7a in which the same test was carried out 5 with a commercially available product which comprises zinc and aluminium particles and a binder comprising a mixture of tetrabutyltitanate and trimethoxyvinylsilane both with and without a top-coat. It is understood that the comparative top-coat is an organic resin comprising phenolic and epoxy 10 components which may in addition comprise up to about 30% by weight of polytetrafluoroethylene (PTFE). It will be noted that the amount of red rust which appears on bolts coated with the comparative base-coat/comparative top-coat combination is significantly greater than for coatings 15 comprising only the comparative base-coat. Furthermore, sets of comparative results shown in Table 7a are also significantly worse than the results in Tables 1,2 and 3.

- 16 -

Table 7a

Comparative Coatings	Time (hours)	% of red rust on head of bolt
Comparative base-coat (2 layers of base-coat only)	240	3.0
	480	6.0
Comparative base-coat + top-coat (2 layers of comp. Base-coat + 1 layer of comp top-coat)	240	16.0

Example 9 - lubrication (with top-coat)

5 [0038] The coefficient of friction of the coated bolts prepared according to Example 8 was analysed as described in Example 5. Testing was performed on bolts having been tightened 1 and 3 times using a steel surface. Coatings 9.1, 9.2 and 9.3 are equivalent to coatings 8.1, 8.4 and 8.5

10 in example 8. The results are shown in Table 8 below:

Table 8 Lubrication (with top-coat B)

Coating	Tightenings	Surface	Coeff. of friction	± variation
9.1	1	Steel	0.117	0.005
9.1	3	Steel	0.117	0.004
9.2	1	Steel	0.122	0.003
9.2	3	Steel	0.124	0.004
9.3	1	Steel	0.127	0.003
5.3	3		0.118	0.003

- 17 -

CLAIMS

1. A coating composition which comprises a binder and a corrosion inhibitor in a solvent, wherein the binder comprises a silicate and an organic titanate, and the corrosion inhibitor comprises aluminium particles and zinc particles.
2. A composition according to Claim 1 wherein the binder comprises 20 to 60% by weight silicate and 40 to 80% by weight organic titanate to a total of 100% by weight.
3. A composition according to Claim 1 or 2 wherein the corrosion inhibitor comprises 80 to 97% by weight of zinc particles and 3 to 20% by weight of aluminium particles to a total of 100% by weight.
4. A composition according to Claim 1, 2 or 3 which further includes an anti-corrosion additive which comprises a metal phosphate.
5. A composition according to any preceding Claim which further includes a lubricant which comprises a hydrocarbon or polytetraethylene wax.
6. A composition according to any preceding Claim which further includes a thickener.
7. A composition according to any preceding Claim having a solid content which comprises 50 to 80% by weight of corrosion inhibitor, 9 to 18% by weight of binder, 0 to 33% by weight of a metal phosphate, 0 to 8% by weight of a lubricant, and 0 to 4% by weight of a thickener.

- 18 -

8. A substrate having a coating which is formed from 1, 2 or 3 coating layer(s) of a composition according to any preceding claim.
9. A substrate having a coating which is formed from 1, 2 or 3 layer(s) of a composition according to any preceding Claim and a further 1, 2 or 3 coating layers of an additional coating composition which comprises 20-25% by weight of a lubricant mixture of phenolic resin, epoxy resin, vinyl butyral resin, and polytetrafluoroethylene, and 70-75% by weight of a solvent mixture of methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone.
10. A substrate having a coating in accordance with claim 8, wherein there is provided a further 1 to 3 layers of a metal particle free top-coat comprising a silicate and an organic titanate in a solvent.
11. A substrate in accordance with any one of claims 8, 9 or 10 wherein the substrate is selected from nuts, bolts and other fasteners, door, bonnet and boot lock parts, hinges, door stoppers, window guides, seat belt components, brake rotors and drums, and other transportation industry related parts.
12. Use of a coating composition according to any one of Claims 1 to 7 for coating a substrate, wherein the substrate is selected from nuts, bolts and other fasteners, door, bonnet and boot lock parts, hinges, door stoppers, window guides, seat belt components, brake rotors and drums, and other transportation industry related parts.

- 19 -

13. A process for providing a substrate with a protective coating comprising applying a composition in accordance with any one of claims 1 to 7 onto the substrate.
14. A process in accordance with claim 13 wherein the coating is formed on the substrate from 1 or 2 coating layer(s) of a composition in accordance with any one of claims 1 to 7, followed by one or both of:-
 - (i) a further 1, 2 or 3 coating layers of an additional coating composition which comprises 20-25% by weight of a lubricant mixture of phenolic resin, epoxy resin, vinyl butyral resin, and polytetrafluoroethylene, and 70-75% by weight of a solvent mixture of methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone and
 - (ii) 1 to 3 layers of a metal particle free top-coat comprising a silicate and an organic titanate.
15. A substrate having a protective coating obtainable by the process in accordance with claim 13 or claim 14.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/05512A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D5/10 C09D183/02 C09D183/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 209 555 A (STEWART JOE W) 24 June 1980 (1980-06-24) column 1, line 34-50 column 2, line 13-22; example 1 ---	1, 3, 6, 8, 13, 15
Y	GB 1 212 424 A (CHANDEN COATINGS INC.) 18 November 1970 (1970-11-18) page 6, line 11-20; claims 1-10 ---	1, 3, 6, 8, 13, 15
A	GB 1 380 748 A (STAUFFER CHEMICAL CO) 15 January 1975 (1975-01-15) cited in the application page 1, line 11-15 page 1, line 33-67 page 3, line 112 -page 4, line 6; example 1 ---	1, 3, 8, 13, 15

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority (claims) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

18 October 2001

02/11/2001

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Girard, Y

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/05512

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4209555	A 24-06-1980	DE	3000731 A1	07-08-1980
		FR	2447394 A1	22-08-1980
		GB	2042575 A ,B	24-09-1980
		JP	55108474 A	20-08-1980
		NL	8000506 A	29-07-1980
GB 1212424	A 18-11-1970	DE	1770378 A1	06-04-1972
		DE	1795673 A1	08-02-1973
		ES	353798 A1	16-10-1969
		FI	48749 B	02-09-1974
		FR	1565235 A	25-04-1969
		NL	6806540 A	13-11-1968
		NO	121069 B	11-01-1971
		NO	132280 B	07-07-1975
		SE	357373 B	25-06-1973
		US	3442824 A	06-05-1969
		US	3546155 A	08-12-1970
GB 1380748	A 15-01-1975	US	3817905 A	18-06-1974
		AT	331515 B	25-08-1976
		AT	765474 A	15-11-1975
		AT	326794 B	29-12-1975
		AT	1093872 A	15-03-1975
		AU	470586 B	20-06-1974
		AU	5031672 A	20-06-1974
		BE	793557 A1	29-06-1973
		CA	996292 A1	31-08-1976
		DE	2258010 A1	09-08-1973
		DK	140107 B	18-06-1979
		FR	2166086 A1	10-08-1973
		IT	974359 B	20-06-1974
		JP	48078235 A	20-10-1973
		NL	7217205 A	03-07-1973
		NO	140892 B	27-08-1979
		SE	392120 B	14-03-1977